

## 4-(Methylsulfanyl)benzaldehyde thiosemicarbazone

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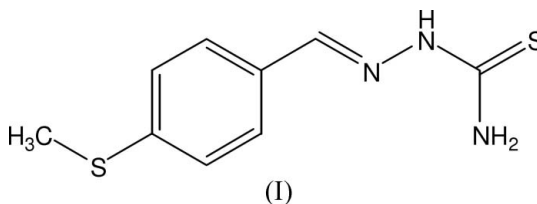
## Key indicators

Single-crystal X-ray study  
 $T = 173$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å  
 $R$  factor = 0.031  
 $wR$  factor = 0.084  
Data-to-parameter ratio = 22.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_9\text{H}_{11}\text{N}_3\text{S}_2$ , crystallizes with two molecules in the asymmetric unit, which differ mainly in the degree of planarity. The  $\text{C}=\text{N}$  double bonds are *trans* configured. Geometric parameters are in the usual ranges. The crystal structure is characterized by  $\text{N}-\text{H}\cdots\text{N}$  and  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds.

## Comment

Thiosemicarbazones (TSCs) of aromatic aldehydes and ketones are widely known as carcinostatic and antimicrobial agents. It has been found that silyl-substituted furfural TSCs possess neurotropic activity (Lukevics *et al.*, 1993). TSCs of arylidene and aryl aldehydes and ketones have shown anti-convulsant activity in maximal electroshock seizure tests (Dimmock *et al.*, 1986, 1990, 1991). In view of the importance of thiosemicarbazones, a new thiosemicarbazone, (I), has been prepared and its crystal structure is reported here.

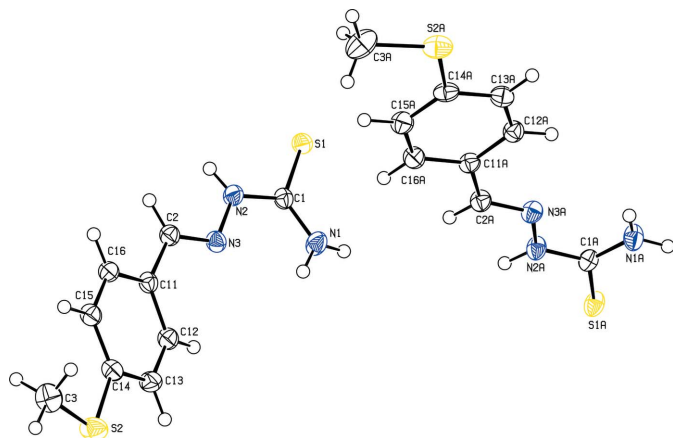


A perspective view of (I) is shown in Fig. 1. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 5.27, November 2005 updated August 2006; *MOGUL* Version 1.1; Allen, 2002). The  $\text{C}=\text{N}$  double bonds are *trans* configured. Whereas one molecule (labelled with suffix *A*) is essentially planar (r.m.s. deviation = 0.062 Å for all non-H atoms) the other one deviates markedly from planarity (r.m.s. deviation = 0.262 Å for all non-H atoms). The methylsulfanyl residues are coplanar with the benzene rings (Table 1). The thiosemicarbazone units are planar (r.m.s. deviation = 0.036 Å for the non-planar molecule and 0.014 Å for molecule *A*), but they form different dihedral angles with the benzene ring, *viz.* 25.19 (4)° for the non-planar molecule and 7.32 (6)° for molecule *A*. Both molecules show an intramolecular  $\text{N}-\text{H}\cdots\text{N}$  contact and two  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds (Table 2). It is remarkable that only the thiocarbonyl S atom acts as an acceptor for hydrogen bonds, while the methylsulfanyl S atom is not involved in hydrogen bonds.

## Experimental

A mixture of 4-methylsulfanylbenzaldehyde (1.52 g, 0.01 mol) and thiosemicarbazide (0.91 g, 0.01 mol) in ethanol (15 ml) was refluxed

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**Figure 1**

Perspective view of the two molecules in the asymmetric unit of the title compound with the atom numbering; displacement ellipsoids are drawn at the 50% probability level.

for 3 h on a water bath. The precipitated solid was filtered, washed with water, dried and recrystallized from acetone (yield: 81%; m.p. 463–465 K). Analysis (%) found (calculated) for  $C_9H_{11}N_3S_2$ : C 47.84 (47.97), H 4.85 (4.92), N 18.54 (18.65), S 28.38 (28.46).

#### Crystal data

$C_9H_{11}N_3S_2$	$V = 1089.76 (10) \text{ \AA}^3$
$M_r = 225.33$	$Z = 4$
Triclinic, $P\bar{1}$	$D_x = 1.373 \text{ Mg m}^{-3}$
$a = 8.2052 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.1947 (5) \text{ \AA}$	$\mu = 0.45 \text{ mm}^{-1}$
$c = 15.5994 (8) \text{ \AA}$	$T = 173 (2) \text{ K}$
$\alpha = 106.558 (5)^\circ$	Block, light orange
$\beta = 97.573 (3)^\circ$	$0.38 \times 0.36 \times 0.33 \text{ mm}$
$\gamma = 100.110 (4)^\circ$	

#### Data collection

Stoe IPDS-II two-circle diffractometer	36432 measured reflections
$\omega$ scans	6421 independent reflections
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	6026 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.847$ , $T_{\max} = 0.865$	$R_{\text{int}} = 0.041$
	$\theta_{\text{max}} = 30.2^\circ$

#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.3428P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.084$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.38 \text{ e \AA}^{-3}$
6421 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
280 parameters	Extinction correction: SHELXL97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.048 (3)

**Table 1**

Selected torsion angles ( $^\circ$ ).

C3–S2–C14–C15	5.08 (12)	C3A–S2A–C14A–C15A	7.41 (12)
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**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1A $\cdots$ S1 <sup>i</sup>	0.873 (17)	2.459 (17)	3.3254 (11)	172.1 (15)
N1–H1B $\cdots$ N3	0.875 (17)	2.266 (16)	2.6364 (13)	105.4 (12)
N2–H2 $\cdots$ S1A <sup>i</sup>	0.854 (17)	2.555 (18)	3.3412 (10)	153.5 (15)
N1A–H1C $\cdots$ S1A <sup>ii</sup>	0.869 (19)	2.604 (19)	3.4707 (11)	174.7 (17)
N2A–H2A $\cdots$ S1 <sup>i</sup>	0.906 (17)	2.454 (17)	3.3499 (10)	169.8 (14)
N1A–H1D $\cdots$ N3A	0.852 (17)	2.302 (16)	2.6440 (14)	104.2 (13)

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $-x + 1, -y, -z$ .

H atoms were found in a difference map. Those bonded to carbon were refined using a riding model, with  $C-H = 0.95 \text{ \AA}$  for aromatic and  $C-H = 0.98 \text{ \AA}$  for methyl groups.  $U_{\text{iso}}(\text{H})$  values were set at  $1.2U_{\text{eq}}(\text{C})$  [ $1.5U_{\text{eq}}(\text{methyl C})$ ]. In addition, the methyl groups were allowed to rotate but not to tip. H atoms bonded to N were freely refined.

Data collection: X-Area (Stoe & Cie, 2001); cell refinement: X-Area; data reduction: X-Area; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PLATON.

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